Electronic Supplementary Material (ESI) for CrystEngComm.

Experimental evaluation of room temperature crystallization and phase evolution of hybrid perovskite materials

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Section 1

Direct comparison method to determine the volume fraction of α and δ phases of $FAPbI_3$

In X–Ray diffraction, the expression for the integrated intensity per unit length of diffraction line is given as [1]

$$I = \left[\left(\frac{I_0 e^4}{m^2 c^4}\right)\left(\frac{\lambda^3 A}{32\pi r}\right)\right]\left[\left(\frac{1}{v^2}\right)[|F|^2 p\left(\frac{1 + cos^2 2\theta}{sin^2\theta\cos\theta}\right)\left(e^{-2M}\right)\right]\left(\frac{1}{2\mu}\right) \qquad \ldots (1)$$

Also can be written as

$$I = \frac{KR}{2\mu} \qquad \ldots (2)$$

$$K = \left[\left(\frac{I_0 e^4}{m^2 c^4}\right)\left(\frac{\lambda^3 A}{32\pi r}\right)\right]; \quad R = \left[\left(\frac{1}{v^2}\right)[|F|^2 p\left(\frac{1 + cos^2 2\theta}{sin^2\theta\cos\theta}\right)\left(e^{-2M}\right)\right]$$

I = integrated intensity per unit length of diffraction line, $I_0 = intensity\ of\ incident\ beam$,

e, m = charge and mass of the electron, c = velocity of light, λ = wavelength of incident radiation,

r = radius of diffractometer circle, A = cross–sectional area of incident beam, v = volume of unit cell,

F = Structure factor, p = multiplicity, θ = Bragg angle, e^{-2M} = temperature factor,

μ = linear absorption coefficient

'K' is independent of nature of the diffracting substance involving only instrumental parameters,

'R' depends on the nature of the materials and phase.

For a two phase material, the expression for the volume fraction analysis can be written as

$$\frac{I_\alpha}{I_\delta} = \frac{R_\alpha C_\alpha}{R_\delta C_\delta} \quad \ldots (3)$$

$I_{\alpha,} I_\delta$ *are the integrated intensities of a specified plane* $(hkl)_\alpha$, $(hkl)_\delta$ *for* α *and* δ *phases respectively*

C_α *and* C_δ volume fraction of α and δ phases respectively such that $(C_\alpha + C_\delta = 1)$

'R' can be found by calculating 'F_{hkl}' of a selected bragg plane for the respective phase

If there exist a third phase of volume fraction C_x in a given material then the volume fraction equation becomes $C_\alpha + C_\delta + C_x = 1$

α–FAPbI$_3$

Cubic crystal structure, lattice parameter (a) = 6.362 Å, space group = P*m*3*m,* volume of the unit cell (*v*) = 257.50 Å ^{3}, multiplicity (p) for highest intensity peak (100) is '6'. The lattice parameters and fractional coordinates (as given below) are obtained from the literature. [2]

Atom	(*u,v,w*)	Highest intensity peak(*hkl*)	*hu+kv+lw*
Pb	(0,0,0)	(100)	0.0
I	(0.5,0,0)	(100)	0.5
C	(0.5,0.57,0.5)	(100)	0.5
N	(0.68,0.47,0.5)	(100)	0.68
H1	(0.5,0.74,0.5)	(100)	0.5
H2	(0.81,0.56,0.5)	(100)	0.81
H3	(0.70,0.31,0.5)	(100)	0.70

The expression for the Structure Factor is

$$F_{hkl} = \sum_{1}^{n} f_n e^{2\pi i(hu + kv + lw)} \quad \ldots (4)$$

F_{hkl} = structure factor of the p lane (*hkl*)

$f_n =$ atomic scattering factor for the atom 'n'

u, v, w are the fractional coordinates of the atom 'n'

$$F_{100} = f_{Pb}\, e^{2\pi i(0)} + f_I\, e^{2\pi i(0.5)} + f_C\, e^{2\pi i(0.5)} + f_N\, e^{2\pi i(0.68)} + f_{H1}\, e^{2\pi i(0.5)} + f_{H2}\, e^{2\pi i(0.81)} + f_{H3}\, e^{2\pi i(0.70)} \qquad \dots (5)$$

The atomic scattering factors can be obtained directly from 'International tables for X-Ray crystallography-Volume III' depending on (sin θ / λ) value.

From Bragg's Law, $2\, d_{100} \sin\theta = n\lambda$ (or) for first order diffraction $(\sin\theta / \lambda) = 1/(2d_{(100)})$

Since α–$FAPbI_3$ is cubic, $d_{(hkl)} = \dfrac{a}{\sqrt{h^2 + k^2 + l^2}}$; $d_{(100)} = 6.362$ Å

Therefore (sin θ / λ) = 0.0785, the nearest value (i.e. 0.1) is taken as the reference for the database to extract atomic scattering factors.

$f_{Pb} = 77.24, f_I = 49.36, f_C = 5.126, f_N = 6.203$ and $f_H = 0.811$

On solving for real and imaginary parts of equation (5) by substituting atomic scattering we obtain the value for F_{100}

$$F_{100} = (19.386) - i\,(7.124)$$

$$|F_{100}|^2 = 426.56 \qquad \dots (6)$$

Now, 'R' can be calculated as follows (for simplification temperature factor considered as constant at room temperature)
From XRD, for (100) Bragg angle 2θ arises at 13.946 degrees

$$(R_\alpha)_{100} = \left[\left(\frac{1}{v^2}\right)[|F|^2 p\left(\frac{1 + cos^2 2\theta}{sin^2\theta \cos\theta}\right)\right] = \left[\left(\frac{1}{(257.50)^2}\right)[(426.56)\,(6)\left(\frac{1.941}{0.0145}\right)\right] = 5.166 \qquad \dots (7)$$

δ–$FAPbI_3$

Hexagonal crystal structure, lattice parameters (a) = (b) = 8.622 Å, c = 7.945 Å, space group = P6$_3$/*mmc,* volume of the unit cell (v) = 511.49 Å^3, multiplicity (p) for highest intensity peak (100) is '6'. The lattice parameters and fractional coordinates (as given below) are obtained from the literature. [3]

Atom	(*u,v,w*)	Highest intensity peak(*hkl*)	*hu+kv+lw*

Pb	(0,0,0)	(100)	0.0
I	(0.830,0.16,0.25)	(100)	0.830
C	(0.384,0.67,0.29)	(100)	0.384
H	(0.506,0.69,0.35)	(100)	0.506
N1	(0.253,0.65,0.39)	(100)	0.253
N2	(0.382,0.67,0.13)	(100)	0.382
H1	(0.133,0.63,0.34)	(100)	0.133
H2	(0.492,0.69,0.06)	(100)	0.492
H3	(0.270,0.65,0.51)	(100)	0.270
H4	(0.276,0.65,0.05)	(100)	0.276

$$F_{100} = f_{Pb}\, e^{2\pi i(0)} + f_I\, e^{2\pi i(0.830)} + f_C\, e^{2\pi i(0.384)} + f_H\, e^{2\pi i(0.5)} + f_{N1}\, e^{2\pi i(0.253)} + f_{N2}\, e^{2\pi i(0.382)} + f_{H1}\, e^{2\pi i(0.133)} + f_{H2}\, e^{2\pi i(0.492)} + f_{H3}\, e^{2\pi i(0.270)} + f_{H4}\, e^{2\pi i(0.276)} \quad \dots (8)$$

For Hexagonal system

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l}{c^2};\ \frac{1}{2d_{(100)}} = 0.196 \approx 0.2 = (\sin\theta / \lambda) \quad \dots (9)$$

Atomic scattering factors extracted from 'International tables for X-Ray crystallography-Volume III' [4] for $(\sin\theta / \lambda) = 0.2$ are

$$f_{Pb} = 68.45, f_I = 42.79, f_C = 3.581, f_N = 4.60 \text{ and } f_H = 0.481$$

On solving for real and imaginary parts of equation (8) by substituting atomic scattering we obtain the value for F_{100}

$$F_{100} = (82.10) - i\,(26.078)$$

$$|F_{100}|^2 = 7420.47$$

Now, 'R' can be calculated as follows (for simplification temperature factor is considered as constant at room temperature)
From XRD, for (100) Bragg angle 2θ arises at 11.77 degrees

$$(R_\delta)_{100} = \left[\left(\frac{1}{v^2}\right)[|F|^2 p\left(\frac{1 + \cos^2 2\theta}{\sin^2\theta\cos\theta}\right)\right] = \left[\left(\frac{1}{(511.49)^2}\right)[(7420.47)\,(6)\left(\frac{1.958}{0.0104}\right)\right] = 32.03$$

$$(R_\delta)_{100} = 32.03 \quad \dots (9)$$

PbI_2

Hexagonal crystal structure, lattice parameters (a) = (b) = 4.557 Å, c = 6.979 Å, space group =P-3m1, volume of the unit cell (v) = 124.63 Å ^{3}, multiplicity (p) for highest intensity peak (001) is '2'. The lattice parameters and fractional coordinates (as given below) are obtained from the literature. [5]

Atom	(u,v,w)	Highest intensity peak(hkl)	$hu+kv+lw$
Pb	(0,0,0)	(001)	0.0
I	(0.333,0.666,0.268)	(001)	0.268

$$F_{001} = f_{Pb}\, e^{2\pi i(0)} + f_I\, e^{2\pi i(0.268)}$$

For Hexagonal system

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l}{c^2} = 0.143; \frac{1}{2d} = 0.189 \approx 0.2 = (sin\,\theta / \lambda)$$

Atomic scattering factors extracted from 'International tables for X-Ray crystallography-Volume III' for ($\sin\theta / \lambda$) = 0.2 are

$$f_{Pb} = 68.45, f_I = 42.79$$

on substituting atomic scattering values in equation (10) we get structure factor for (100) plane of PbI_2

$$F_{001} = (63.66) - i\,(42.516)$$

$$|F_{100}|^2 = 5859.61$$

Now, 'R' can be calculated as follows (for simplification temperature factor is considered as constant at room temperature)
From XRD, for (001) Bragg angle 2θ arises at 12.674 degrees

$$(R_x)_{001} = \left[\left(\frac{1}{v^2}\right)[|F|^2 p\left(\frac{1 + cos^2 2\theta}{sin^2\theta \cos\theta}\right)\right] = \left[\left(\frac{1}{(124.637)^2}\right)[(5859.61)\,(2)\left(\frac{1.951}{0.0119}\right)\right] = 123.691 \quad \ldots (11)$$

$$(R_x)_{001} = 123.691 \quad \ldots (12)$$

For the 2 min dipping sample (PbI_2 film dipped in FAI solution for 2 min) the volume fraction calculation as follows:

First evaluate the integrated intensity of the Bragg plane under consideration and then substitute R values to get the volume fractions of respective phases.

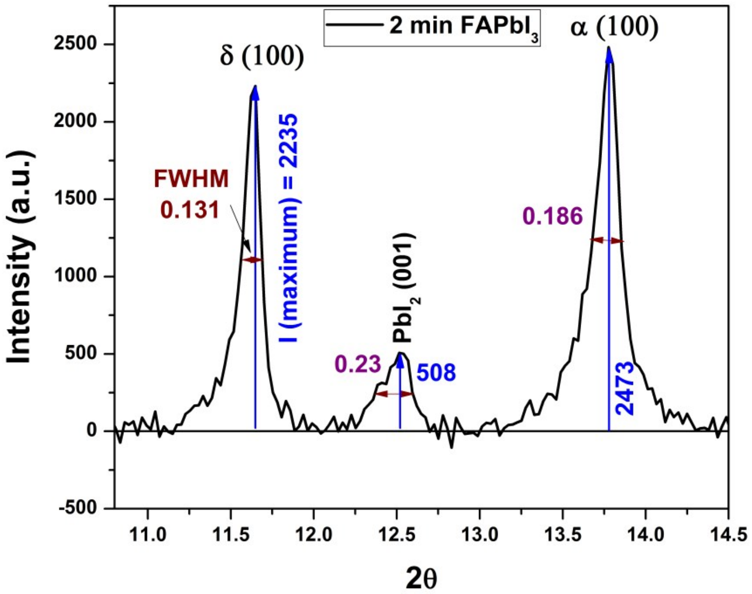

Fig 1 XRD pattern showing characteristic peaks of α and δ of $FAPbI_3$ and PbI_2 for the sample PbI_2 film dipped in FAI solution for 2 min.

Integrated Intensity = product of I(maximum) and FWHM. [6]

From the above figure the calculated integrated intensities are

$I_\alpha = 459.97$; $I_\delta = 292.78$; $I\ (PbI_2) = I_x = 116.84$

Rewrite the equation (3) as

$$\left(\frac{I_\alpha}{I_\delta}\right)\left(\frac{R_\delta}{R_\alpha}\right) = \frac{C_\alpha}{C_\delta}$$

For I_α (100), I_δ (100)

$$\frac{C_\alpha}{C_\delta} = \left(\frac{I_\alpha}{I_\delta}\right)\left(\frac{R_\delta}{R_\alpha}\right) = \left(\frac{459.97}{292.78}\right)\left(\frac{32.03}{5.166}\right) = 9.740$$

$$C_\delta = 0.102\ C_\alpha \qquad \ldots (13)$$

and

$C_x\ is\ the\ volume\ fraction\ of\ PbI_2$

$$\frac{C_\alpha}{C_x} = \left(\frac{I_\alpha}{I_x}\right)\left(\frac{R_x}{R_\alpha}\right) = \left(\frac{459.97}{116.84}\right)\left(\frac{123.69}{5.166}\right) = 94.25$$

$$C_x = 0.010\, C_\alpha \qquad \ldots (14)$$

Since

$$C_\alpha + C_\delta + C_x = 1 \qquad \ldots (15)$$

On solving equations (13), (14) and (15) we get the following values for the volume fraction

$C_\alpha = 0.8992 = 89.92\%$

$C_\delta = 0.09171 = 9.17\%$

$C_x = 0.008992 = 0.89\%$

The volume fraction for other compositions is calculated in the similar way as described above. A tabular column is given in the main draft mentioning the volume fraction of various phases for $FAPbI_3$ for various dipping times.

Table 1 Calculated integrated intensities (I), R values and volume fraction (C) of various phases with respect to the dipping time with formula F1.

Dipping time	R_α (a.u.)	I_α (a.u.)	R_δ (a.u.)	I_δ (a.u.)	R_x (a.u.)	I_x (a.u.)	C_α (%)	C_δ (%)	C_x (%)
30 sec	5.166	268.94	32.03	0.0	123.69	1532.49	80.77	0.0	19.22
2 min	5.166	459.97	32.03	292.78	123.69	116.84	89.92	9.17	0.89
10 min	5.166	446.20	32.03	667.19	123.69	140.524	79.74	19.21	1.04
20 min	5.166	334.88	32.03	682.0	123.69	0.0	75.27	24.72	0.0
40 min	5.166	344.90	32.03	1177.12	123.69	0.0	64.49	35.50	0.0

*a.u. – arbitrary units

Section 2

Curve fitting parameters

(i) Formula, F1, δ–$FAPbI_3$

Equation y = A1 - A2*exp(-k*x) ~ $A_1(1-\exp(-kx)) \Rightarrow C_\delta = A_1(1-\exp(-kt))$
[here $y=C_\delta$; x = t]

Adj. R-Square 0.93012

	Value	Standard Error
A1	37.97491	7.39878

A2	36.06563	7.00155
k_1	0.05943	0.03035

(ii) Formula, F2, δ–$FAPbI_3$

Equation $y = A1 - A2*\exp(-k*x)$ ~ $C_\delta = A_1(1-\exp(-kt))$; [here $y=C_\delta$; $x = t$]

Adj. R-Square 0.90941

	Value	Standard Error
A1	107.26697	131.84
A2	107.1345	129.27794
k_2	0.01648	0.02783

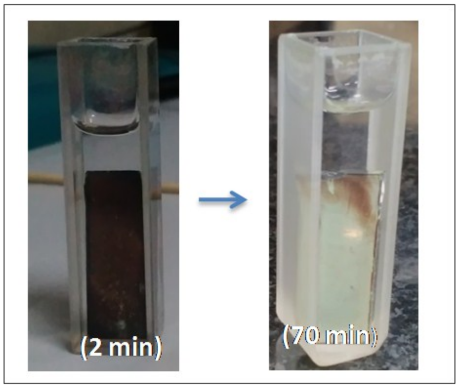

Figure S1. PbI_2 film dipped in FAI solution for 2 min and for 70 min dipping

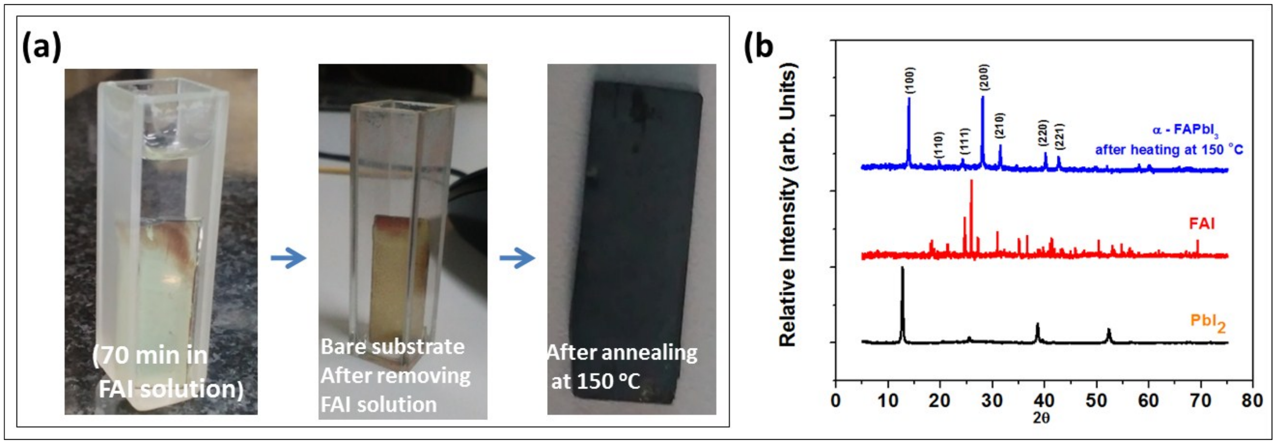

Figure S2 (a) conversion of yellow FAPbI3 into black FAPbI3 (b) XRD patterns of PbI2, FAI and heated FAPbI3 at 150 oC forming α–phase.

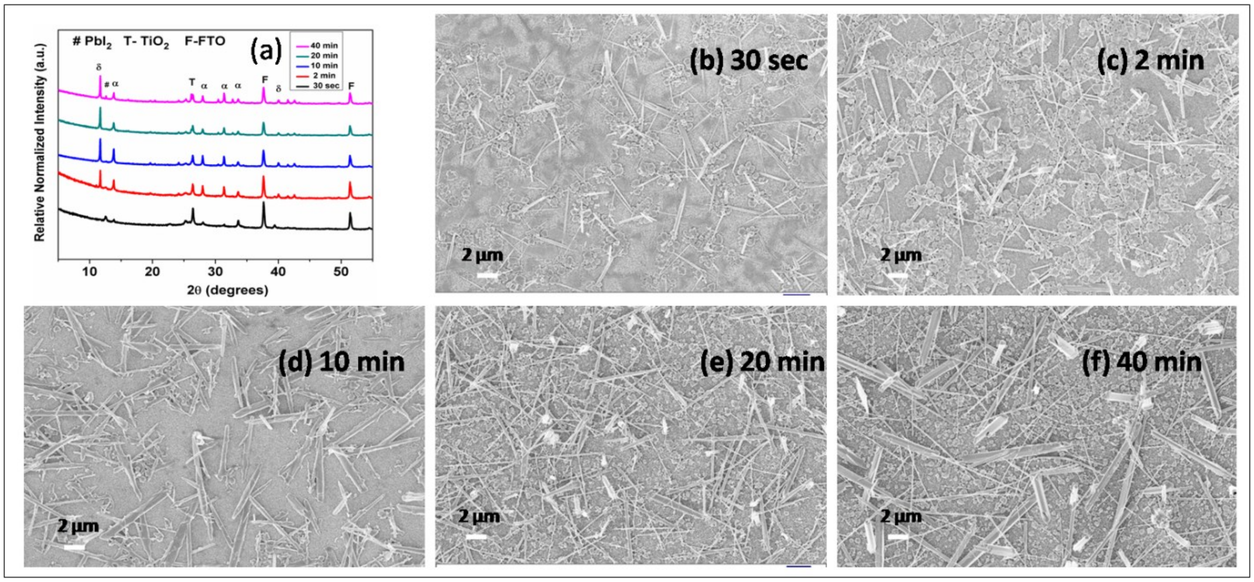

Figure S3. Phase and microstructure information of PbI_2 substrates dipped in FAI solution (formula, F2 where antisolvent toluene is replaced with chlorobenzene) (a) XRD of $FAPbI_3$ formation with dipping time, (b-f) FEG-SEM images of PbI_2 converted into $FAPbI_3$ with different dipping durations of 30 sec (b), 2 min (c), 10 min (d), 20 min (e) and 40 min (f).

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